TITLE: Development of Multi-Task Catalysts for Removal of $NO_X$, and Toxic Organic Compounds during Coal Combustion

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**ABSTRACT**

**OBJECTIVE**

The goal of this project is to develop a catalyst for the oxidation of volatile organic compounds (VOC) and the reduction of NO in the presence of $SO_x$ and trace metals. Three primary objectives are described below:

1. Synthesis and characterization of selected polyoxide supports
   - Integrate the synthesis of polyoxide supports
   - XRD, Raman IR, FTIR, $NH_3$-TPD, BET surface area and pore size distribution
   - Develop a method to quantitatively determine the amounts of the anatase and rutile phases of titania in polyoxide supports
   - Identify the valence state of vanadium in the precursor solution using UV/VIS spectrometry

2. Catalytic experiments with synthetic flue gases
   - Catalytic screening
   - Effects of $H_2O$ and $SO_2$ on performance

3. Catalytic performance with actual flue gas generated from a coal combustor
   - Effects of trace metals
   - Simulate industrial conditions

**ACCOMPLISHMENTS TO DATE**

A number of mixed oxide supports have been synthesized from both organic and inorganic precursors by sol-gel co-precipitation, and our work investigated the effect of synthesis parameters. Vanadia was added to the supports using wet

impregnation methods. Catalytic tests were performed with a "synthetic" flue gas containing NO, $O_2$, and $NH_3$ (reductant), and benzene was introduced as the VOC. Benzene conversion increased with temperature when only benzene, oxygen (2000 ppm), and helium were fed to the reactor. Benzene conversion rose to 98% at 400 ºC when sufficient oxygen was provided to the system. The presence of benzene did not hinder the $DeNO_x$ performance of our catalytic system, and nitrogen selectivity actually increased in the presence of benzene at higher temperatures. The presence of SCR components also elevated benzene conversion above the levels measured when only benzene, oxygen, and helium were present. Finally, the oxidation of benzene was not significantly affected by the concentration of benzene in the feed stream up to 8 ppm.

It is remarkable to note that the valence of vanadium in the precursor solution during the impregnation step is crucial for the synthesis of efficient $DeNO_x$ catalysts. More specifically, $V^{5+}$ in the precursor solution yields lower-performance catalysts compared to the case of $V^{4+}$. Aging the vanadium precursor solution, which is associated with the reduction of $V^{5+}$ to $V^{4+}$ ($VO_2^+ \rightarrow VO^{2+}$) via the following reaction scheme, results in catalysts with excellent catalytic behavior under identical activation and operating conditions.

$$2NH_4VO_3 \xrightarrow{[COOH]_2} 2[COONH_4] + 2OH^- + 2VO_2^+ \text{ (yellow)} \tag{1}$$

$$C_2O_4^{2-} \longrightarrow 2e^- + 2CO_2 \tag{2}$$

$$VO_2^+ + 2H^+ + e^- \longrightarrow H_2O + VO^{2+} \text{ (blue)} \tag{3}$$

The present variation of loading vanadia is used for $TiO_2$-based supports with low crystallinity. These supports, which have traditionally performed poorly, are now able to function as effective SCR catalysts. Increasing the acidity of the support by incorporating oxides such as $WO_3$ and $Al_2O_3$ significantly improves the SCR activity and nitrogen selectivity. The concentration of tungsten used in these catalysts was higher than that typically used in industry. It was also found that for the synthesis of the above catalysts, the supports should be synthesized with the simultaneous precipitation of the corresponding precursors. From our work we found that the mixed oxide catalysts possess Brønsted and Lewis acid sites of comparable strength over a wide range of temperatures. Catalysts prepared from aged vanadium precursor solutions demonstrated a wider temperature interval for optimum operation. FT-IR, $NH_3$-temperature programmed desorption, XRD, Raman-IR, and UV/VIS are being used to characterize the catalysts used in this work.

## SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

A great opportunity exists to utilize the abundant coal reserves present in the U.S. in a clean and efficient manner to help meet future energy needs. The simultaneous catalytic removal of $NO_x$ and VOC in the presence of $SO_x$ and trace metals will help meet future emissions regulations for coal utilization. In addition, simultaneous removal offers potential cost savings by incorporating two processes in a single step. Catalytic methods do not require the substantial energy input of thermal methods, nor do they generate the large solid waste streams inherent in absorption processes. Therefore, catalytic methods provide the best starting point for flue gas treatment that will allow the continued use of coal in the midst of increasingly stringent emissions regulations.

## PLANS FOR THE COMING YEAR

- Quantitative studies of vanadium's valence state in the precursor solution to better understand the increased catalytic activity of low $TiO_2$ crystallinity supports.
- Mechanistic studies using in-situ FTIR coupled with mass spectrometry
- Complete characterization of synthesized supports (Raman-IR, etc.)
- Compare the catalytic performance of supports impregnated with $V^{+2}$, $V^{+3}$, $V^{+4}$, and $V^{+5}$ in the precursor solution
- Coal combustor start-up and optimization of combustion parameters

# Articles, Presentations, and Students Receiving Support from the Grant

**Journal Articles (peer reviewed)**

1) Economidis N. V., Peña, D. A., and Smirniotis, P. G. "Comparison of $TiO_2$-based Oxide Catalysts for the Selective Catalytic Reduction of NO: Effect of Aging the Vanadium Precursor Solution", *Applied Catalysis B: Environmental*, (accepted for publication) 1998.

**Conference Presentations**

1) Peña D. A., Jenkins, R. G., and Smirniotis, P. G. "Investigation of the Valence State of Vanadium during Impregnation for the SCR of NO using $NH_3$", presented at The Tri-State Catalysis Society Spring Symposium, Louisville, KY, April 20-21, 1999.

2) Peña D. A., Jenkins, R. G., and Smirniotis, P. G. "The Role of V Valence State in the Precursor Solution of $DeNO_x$ Catalysts", to be presented at The 16th North American Meeting of the Catalysis Society, Boston, MA, May 30-June 3, 1999.

3) Peña D. A., Jenkins, R. G., and Smirniotis, P. G. "Investigation of the Valence State of Vanadium during Impregnation for the SCR of NO using $NH_3$", to be presented at The 12th International Congress on Catalysis, Granada, SPAIN, July 9-14, 2000.

**Students Receiving Support from the Grant.**
*Graduate Students:*
1) Mr. Donovan Peña, graduate (Ph.D.) student in Chemical Engineering
2) Mrs. Elizabeth Allen, graduate (M.S.) student in Chemical Engineering
3) Mr. Tianxin Zhang, graduate (M.S.) student in Chemical Engineering

4) Mr. Scott Blatnik, undergraduate (Senior) student in Chemical Engineering